**MSL/SAM MEASUREMENTS OF NITROGEN AND ARGON ISOTOPES IN THE MARS ATMOSPHERE.** Michael H. Wong[1,2], Sushil K. Atreya[1], Paul R. Mahaffy[3], Melissa Trainer[3], Heather Franz[3], Jennifer Stern[3], Tobias Owen[4], Chris McKay[5], John Jones[6], Heidi Manning[7], Rafael Navarro-González[8]. [1]University of Michigan, [2]University of California, [3]NASA GSFC, [4]University of Hawaii, [5]NASA ARC, [6]NASA JSC, [7]Concordia College, [8]UNAM.

**Introduction:** We report on three QMS (part of MSL/SAM*) measurements of the martian atmosphere in the first 100 sols. Consistent results are obtained for the isotopic ratios of $^{14}N/^{15}N$ and $^{40}Ar/^{36}Ar$, although these measurements are still preliminary. An enrichment experiment will permit better measurements of minor isotope ratios by scrubbing $CO_2$ from the sample [1]. Table 1 summarizes our preliminary nitrogen and argon isotope measurements and upper limits.

**Measurements:** The analysis described here uses two QMS modes for scanning the mass range: unit scan and fractional scan modes [1]. Details of the analysis methods are given in [2].

Figure 1 shows the m/z 14 signal (from $^{14}N^+$ and $^{14}N^{14}N^{++}$) and m/z 14.5 (from $^{15}N^{14}N^{++}$). For molecular nitrogen, the primary ion at mass-to-charge ratio m/z 28 cannot be used because both $CO_2$ and CO also contribute to the signal at m/z 28. The m/z 15 signal is not significantly above the background, so we do not measure $^{15}N^+$ or $^{15}N^{15}N^{++}$.

Significant signal at m/z 14.5 will allow a measurement of the $^{14}N/^{15}N$ ratio. Different behavior at m/z 13.5 and 14.5 clearly demonstrates that the fractional mass data (at both masses) are not contaminated by signal at the adjacent integer masses.

Experiments in Table 1 each followed a different measurement sequence, with varying durations of background and sample scans, fractional and unit scans, volume expansions, and ionization filament current levels [1, 2]. For example, the experiment on Sol 77 consisted of a QMS background scan, a gas manifold background scan, and two scans at full atmospheric pressure, each followed by a manifold background scan (Fig. 2). This sequence allowed accurate characterization of the time-varying background and sample signal levels. The best MSL $^{14}N/^{15}N$ upper limit is an average of all three experiments, and the best MSL $^{40}Ar/^{36}Ar$ ratio is a preliminary SAM team consensus from Sol 77 data.

Nitrogen isotope ratios in Table 1 are given as upper limits, because we have not yet constrained the $N^+/N_2^{++}$ splitting fraction in the QMS. Figure 3 shows the $^{14}N/^{15}N$ ratio derived from SAM data at m/z 14 and 14.5, as a function of this splitting fraction. If the SAM calibration gas (black line) had a terrestrial $^{14}N/^{15}N$ ratio of 272 (dashed black line), then the $N^+/N_2^{++}$ splitting fraction must be 2/3, implying that SAM measured $^{14}N/^{15}N = 94$ on Mars. The SAM $N^+/N_2^{++}$ splitting fraction would have to be 2/5 if the Viking measurement of $^{14}N/^{15}N = 170$ is correct, which would be the case only if the calibration gas had $^{14}N/^{15}N = 490$. We will independently determine the $^{14}N/^{15}N$ ratio in our calibration gas, to constrain the $N^+/N_2^{++}$ splitting fraction.

Uncertainties in the values listed in Table 1 include statistical noise, background uncertainty, and uncertainty from time-variation in the signal. Systematic sources of error are still being discovered and characterized, so these estimates are preliminary. Large in-

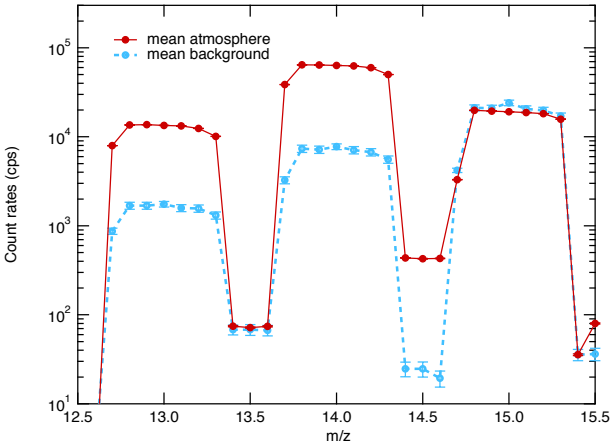


**Figure 1:** SAM/QMS spectrum at 0.1-Da resolution, acquired on Sol 77 of the MSL mission. Background and atmosphere spectra are averages of many scans, and statistical uncertainties plotted as error bars.

**Table 1:** Preliminary nitrogen and argon isotopic ratios and limits from SAM/QMS. Viking data from [3].

| MSL Sol† | $^{14}N/^{15}N$ | $\delta^{15}N$ (‰) | $^{40}Ar/^{36}Ar$ |
|---|---|---|---|
| 18 | < 249 ± 47 | > 93 | 217 ± 80‡ |
| 45 | < 256 ± 22 | > 65 | 2020 ± 460 |
| 77 | < 285 ± 12 | > –45 | 1900 ± 300 |
| (Viking) | 170 ± 15 | 600 ± 155 | 3000 ± 500 |
| **Best MSL:** | **< 277 ± 10** | **> –18 ± 37** | **1900 ± 300** |

* MSL = Mars Science Laboratory, SAM = the Sample Analysis at Mars instrument suite, QMS = Quadrupole Mass Spectrometer.

† MSL Sol 0.0 corresponds to UTC 2012-08-05 13:50. For detailed SAM atmospheric experiment timing, see [4].

‡ Results on Sol 18 were contaminated by terrestrial air.

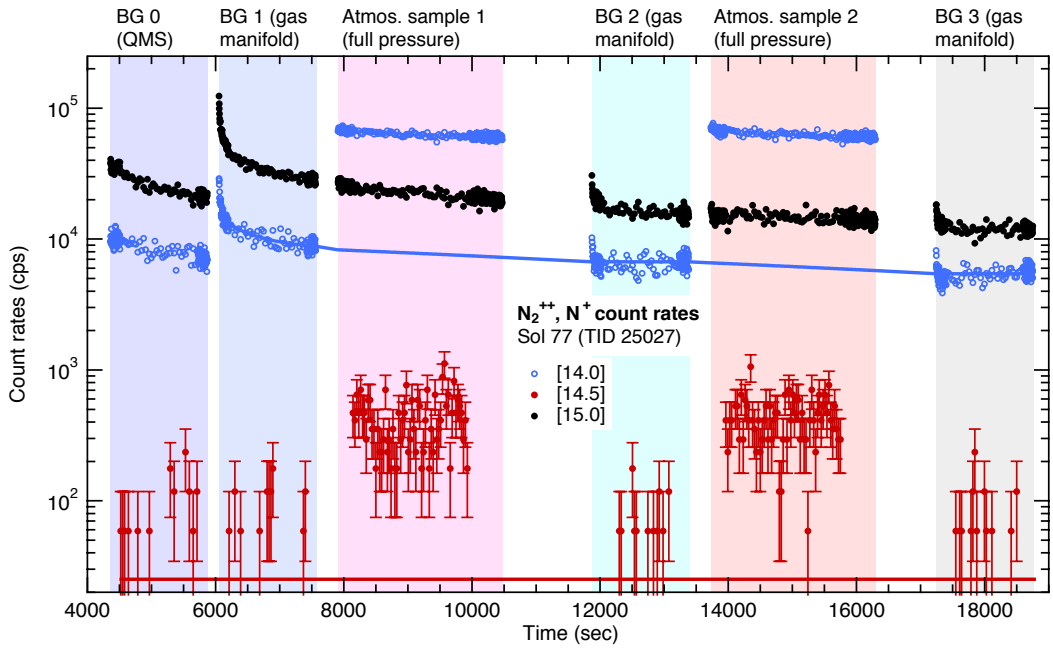


**Figure 2:** SAM/QMS background and atmosphere scans for Sol 77, with both fractional and unit scan data plotted [2]. Data at m/z 14 and 14.5 were used to derive an upper limit of $^{15}N/^{14}N < 285$. Error bars for m/z 14.5 are based on Poisson detector noise; this noise component is < 1 % for higher counting rates at m/z 14 and 15. The m/z 15 signal is not significantly above the background level. Continuous lines indicate background corrections for m/z 14 and 14.5. For mass 14, a time-varying background can be measured. For mass 14.5, any time variation is smaller than the uncertainty in the mean value of the background level, so a constant background correction is used.

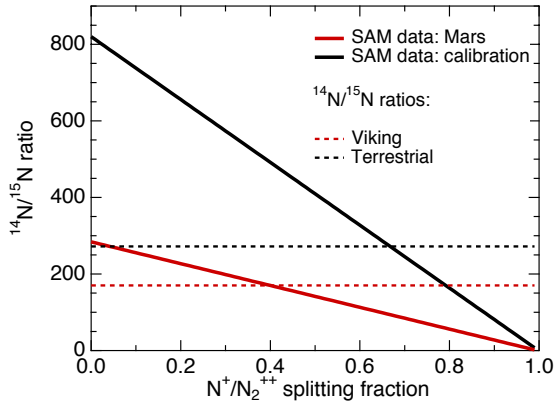


**Figure 3:** Nitrogen isotopic ratio as a function of the $N^+/N_2^{++}$ splitting pattern (an intrinsic characteristic of the SAM/QMS). With terrestrial $^{14}N/^{15}N$ in the calibration gas, the splitting fraction lies at the intersection of the black lines. A planned measurement of the calibration gas isotopic ratio will derive the splitting f,raction determining $^{14}N/^{15}N$ on Mars from the solid red line.

creases in signal to noise are anticipated with the SAM enrichment experiments [1]. Once the SAM $N^+/N_2^{++}$ splitting fraction is determined for nitrogen, we will convert the upper limits into measured values.

**Discussion:** MSL/SAM results for both the $^{40}Ar/^{36}Ar$ isotope ratio and the Ar/N ratio are significantly different from the Viking measurements [2]. These ratios should not vary in time, so it is likely that systematic errors affect one or both retrievals [5]. The difference with respect to Viking has implications for analyses of gas inclusions in meteorites which use the Ar/N ratio and N isotopes to indicate the degree of mixing between the martian atmosphere and internal gas component due to the shock of impact ejection (e.g., [6]). Nitrogen isotopic ratios in martian meteorites imply a Mars atmospheric $^{14}N/^{15}N < 210$ [7]. Regardless of the SAM $N^+/N_2^{++}$ splitting fraction, the upper limits in Table 1 are consistent with the meteorite data.

The SAM measurements—once confirmed by further laboratory testing and the enrichment experiment—will provide new constraints on the evolution of the atmosphere of Mars [8].

**References:** [1] Mahaffy, P.R. et al. (2012) *SSR 170,* 401–478. [2] Franz, H. et al. (2013a) *LPS XLIV*. [3] Owen, T. (1992) In *Mars,* pp. 818–834. [4] Wong, M.H. et al. (2013b) *LPS XLIV*. [5] Atreya, S.K. et al. (2013) *LPS XLIV*. [6] Aoudjehane, H.C. et al. (2012) *Science, 338,* 785–788. [7] Bogard, D.D. et al. (2001) *Chron. Evol. Mars 96*, 425–458. [8] Jones, J.H. et al. (2013) *LPS XLIV*.